A STUDY OF THE "CRACKING" OF PETROLEUM

BY

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F. W. HOOK

ARMOUR INSTITUTE OF TECHNOLOGY

1914

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A STUDY OF

THE "CRACKING" OF PETROLEUM.

A THESIS

Presented by

CLARK CABLE HERITAGE,

FRANK WILLIAM HOOK.

To The

PRESIDENT AND FACULTY

of

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

HAVING COMPLETED THE PRESCRIBED COURSE OF STUDY IN

CHEMICAL ENGINEERING

1914.

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APPROVED: W.M. McCormack
Professor of Chemical Engineering.

APPROVED: F.M. Raymond
Dean of the Engineering Studies.

L.C. Morin.

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PREFACE.

The time has come when the demand for greater efficiency, both in manufacture and labor, is foremost. It is of vital importance to the manufacturer to obtain the greatest posible returns from his industry, and he is constantly endeavoring to cut down the working loss by utilizing what has, in the past, been considered "waste", or if not waste, a product of minor value. It becomes then the prime function of the Chemical Engineer to find some more valuable product and then to design some means by which it may be economically manufactured and consumed.

The technology of petroleum distillation offers many problems, in which are linked some of the most interesting phenomena of Chemistry together with the fundamental principles of engineering, which facts render the subject interesting and valuable to one whose profession is Chemical Engineering. These considerations

primarily led to the choice of this thesis.

It is of course understood that the whole field of petroleum distillation could not be treated in the briefest manner in the short space of two months and therefore some particular phase had to be chosen. The intense interest which has been centering about the economics of gasolene since the advent of the internal explosion engine, -- not the problem of the internal combustion engine which includes the Diesel type, -- recommended to our attention and for our work this particular phase of increased gasolene production.

The library work was accomplished at the library of the Armour Institute of Technology and at the Crerar Library, in neither of which were found any books devoted entirely to the cracking phenomenon, its history and development. Neither have there been published any up-to-date books upon the whole subject of petroleum with the exception of Sir Boverton Redwood's work of

1913. That these volumes of Redwood are excellent every one knows. The only available petroleum periodical was "Petroleum", a German magazine. Many articles abstracted from the "National Petroleum News", published in Cleveland, and the "Petroleum Review", published in London, were not available, though the former graciously forwarded to the authors one copy especially desired. There is very little material in the current literature on cracking in comparison with the great wealth of patents in all countries which have been granted in the last decade, due to the rise of the automobile industry.

The difficulties encountered in maintaining distillation around 300° C. and higher, due to leaking stills and joints, were many. It is hoped that the reader will be lenient in judging the following pages because of these difficulties, the short time available for work and the inexperience of the investigators.

It is assumed that the reader is familiar

with the principles of Chemical Engineering and organic chemistry. The authors wish to mention the names of Professor H. McCormack, Dr. C. A. Tibbals, and Asso. Professor B. B. Freud as lending aid in various points throughout the thesis.

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INTRODUCTION.

The study of this phenomenon of petroleum cracking has been carried out under two general heads of library work and laboratory work. In the former is included first a brief treatise on the general principles and important factors, second a short resumé of a historical nature with references on the cracking process in America, and third a complete review with patent references of other devices for producing light hydrocarbons by modifying the distillation.

Under the head of laboratory work is included first the object sought in undertaking the laboratory work, and the general scheme of attack; second, the apparatus used; third, the methods of analysis; fourth, the actual work done on the two petroleums available, with results and tables; and fifth, some comparative analyses on commercial gasolene and motor spirit purchased at random.

I.

GENERAL.

It seems fitting to introduce a general discussion of cracking by first defining the various terms which will be used throughout the work. By petroleum will be meant the crude oil as it leaves the well; and the various fractions of petroleum on distillation we will term crude naptha below 150° or below 0.750 gravity; burning oil 150°-300° or below 0.850 gravity; and lubricating oil over 300°. All temperatures given are Centigrade throughout unless designated Fahrenheit.

The crude naptha on steam distillation yields three grades of napthas and gasolene. There are many grades of gasolene on the market with gravities varying from 0.700 down to 0.635 and we will designate gasolene that natural distillate not due to cracking which is cut within these limits. Gasolene really should not be valued upon its gravity according to Mr. Tipper

of the Texas Oil Co. (1), but rather its boiling point and endpoint. He makes the astounding statement that a Pennsylvania fraction of 0.705 gravity will possess no more volatility from the standpoint of low boiling point and low end point than a California fraction of 0.745 gravity. He concludes that the gravity is then of no value as a test for three reasons: first, the gravity varies according to the state in which the fraction is produced and also in which it is sold; second, the gravity and volatility have no connection; third, one gravity cannot be stated for all fractions of the same fuel value. The term petrol is the foreign nomen for the American word gasolene and will only be used in this work when quoting from foreign articles.

One more important distinction needs to be emphasized and that is the difference between gasolene and motor spirit. By motor spirit we shall mean that volatile fraction of petroleum for use in engines which has been produced by

(1) National Petroleum News, V.5, No. 5, p.44.

cracking, by blending, by compression of natural gas, or in any other way besides strict fractional distillation. It is almost needless to say that motor spirit is inferior to gasolene, for the former has a distillation curve full of breaks, while the latter maintains a regularly ascending distillation curve. The latter will then be much more effective and easier to vaporize though its boiling point be higher as a whole than that of the motor spirit as a whole.

All gravities will be given in terms of an equal volume of water at greatest density and for the benefit of readers using the Baumé scale, which is both inaccurate and inconvenient, the following conversion formulae are inserted here:

From Baumé to gravity: $\frac{140}{130 - Be} = Gr.$

From gravity to Baumé: $\frac{140}{Gr} - 130 = Be$

Petroleum is chemically an extremely varied mixture of hydrocarbons both aliphatic and aromatic of greatly varying degrees of stauration.

Brannt[1] says that members of all the series from C_nH_{2n+2} down through the olefins and acetylenes to the very unsaturated series C_nH_{2n-12} have been found together with many of the napthene group such as C_6H_6, C_6H_{12} to C_8H_{10}, and C_8H_{16} to $C_{15}H_{30}$. In considering the cracking phenomenon it is hardly necessary to take cognizance of any of these series, except the paraffins and olefines although it is well within the range of possibilities that the latter may be cracked to more unsaturated series. Benzenes cannot be cracked however.

Before proceeding further it would perhaps be well to define this term which is used so glibly by every one. Cracking is essentially a destructive distillation of certain heavier portions of the petroleum by heating them above their normal boiling points in either of three ways: first, and simplest, by using a rather tall still so that the upper portion will be cool enough to condense the heavier vapors which

[1] Petroleum, Its history, Origin, etc. 1895 (Book)

will then drop back into the much hotter body of petroleum yet remaining in the still and will thus be decomposed; second, by applying pressure to the still so that the forced boiling point will be much in excess of the normal boiling point and somewhat in excess of the decomposition point; and third, by subjecting the vapors produced in an ordinary still to heat from some other external source in a second still or receptacle. It is thus easily seen that many mechanical factors bear on the products obtained, chief among which are the design of still, the temperature maintained and the length of the campaign. It is generally understood, according to Redwood[1] that even the products of a careful fractional distillation are not those in the original oil.

These new products obtained vary therefore greatly and may be made anything from the very small changes induced in a fractional distillation to a complete dissociation to Carbon and

[1] Treatise on Petroleum, 1913, V.II,p.7.

Hydrogen. Of course the ideal conditions are those which make the resulting product a maximum of light distillate with a minimum of permanent gases and coke. Thorpe and Young[1] in experimenting in 1871 by heating solid paraffins under pressure obtained very little gas and "an almost perfect change to liquid products of an olefinic nature". They therefore wrote the following type reaction which they believed expressed the whole reaction:-

$$C_nH_{2n+2} \xrightarrow{\text{heated}} C_{n-x}H_{2(n-x)} + C_xH_{2x}$$

As a matter of fact, as shown above, the products may be of any phase and any degree of unsaturation. It is then the problem to so regulate the degree of heating , acceleration of heating, and design of still and flues so that the lightest yet least unsaturated products will result. Brannt[2] states that beside the light

(1) Proceedings, Royal Society, XIX, 370
(2) Petroleum, its History and Origin.

hydrocarbons formed by the decomposition, there is also produced a corresponding quantity of heavy hydrocarbons not originally present, the proportion between the two being quite constant, (i.e. the more of the lighter the more of the very much heavier.)

Another practical point arises in the probable burning of the vapors[1] which augments the difficulties of deodorizing and bleaching the product. The temperature of the still top must be high enough to allow a certain flow of distillate but not high enough to burn the vapors as they come in contact with the sides of the still.

The practicability of the process depends on the demand and supply of gas oil and lubricating oil on the one hand and motor spirit on the other, together with various questions of greater fuel consumption and investment in this process. The fuel consumption is said to be five times as great for a cracking distill-

[1] Petroleum Distillation, A.N.Leet, 1885.

ation as for a fractional one due not only to the greater length of time but to the endothermal nature of the reaction.

HISTORICAL.

The three methods by which petroleum may be cracked as mentioned on pages 4 and 5 originated in two different countries, the simple slow condensation and dropping back into the still in the United States; the external heating in tubes and the pressure distillation in England. In a report on Petroleum by S. F. Peckham in 1885, he says"The earliest practical application of the destructive distillation of petroleum was in the manufacture of illuminating oil by Luther Atwood of Boston, Mass. in 1859." (1) This was in connection with the Downer Kerosine Co., who are said to have worked up thousands of barrels of heavy petroleum before it really was an article of commerce. If this is true, the "accidental discovery" is robbed of its importance though still an interesting tale.

(1) Tenth Census, U.S. (1880)

The story of this accidental discovery in a New Jersey refinery, "one cold afternoon in Nov. of 1865", when the still man went home to dinner and on being taken with a fit did not return until late in the afternoon, when he found a fraction of astonishingly light gravity issuing from the condensers,-- is familiar to any one who has read any of the oil literature (1) at all. The proprietor later had a glass still built in which he studied the phenomenon and discovered the process of condensation on the upper part of the still and consequent dripping back. There never were any patents granted on this and as the information spread, all distillers were soon remodeling their stills to utilize the new idea, by simply uncovering the upper half which had previously been bricked over, the original idea in distillation being to carry out the operation in the least time, thus economizing fuel.

This American process has been used universally since its accidental discovery with more

(1) For full details see Petroleum Distillation, Chap II, A.N.Leet.

or less change in still design, the tendency being to elongate the still vertically and even use dephegmators on top, to facillate condensation. In 1895, Brannt[1] describes the process then in vogue as being carried out in stills constructed especially for this purpose. The upright form was the most suitable because the vapors, having to traverse a long distance in the still itself, have a chance to condense partially and in flowing back on the overheated sides to suffer decomposition and vaporization. The still was therefore provided with a large condensing dome and suitable dephlegmator, the use of the latter being absolutely necessary to increase the yield. They were so arranged that the oil vapors met large condensing surfaces, that the heavy liquid all flowed back into the still, and only the most volatile portion went over. The material of the still was manganese iron and the height was two to two and

(1) Petroleum, Its History and Origin.

one-half times the diameter. The flues are so arranged that the heat can be admitted to all the still walls during the early part of the distillation and later cut off from the upper part to facilitate the cracking.

An address by F. C. Robinson[1] of the Atlantic Refining Co. gives the procedure which his company is using. Petroleum is pumped into stills containing 500 to 1000 barrels, which consist simply of horizontal steel cylinders made of sheets of ½" boiler steel riveted together and provided with manholes in top and ends, with petroleum line, vapor line, safety valve, combustion chamber, and flues, fractional air condenser, water condensers, and gas exit pipe. The following table gives the data on a run:-

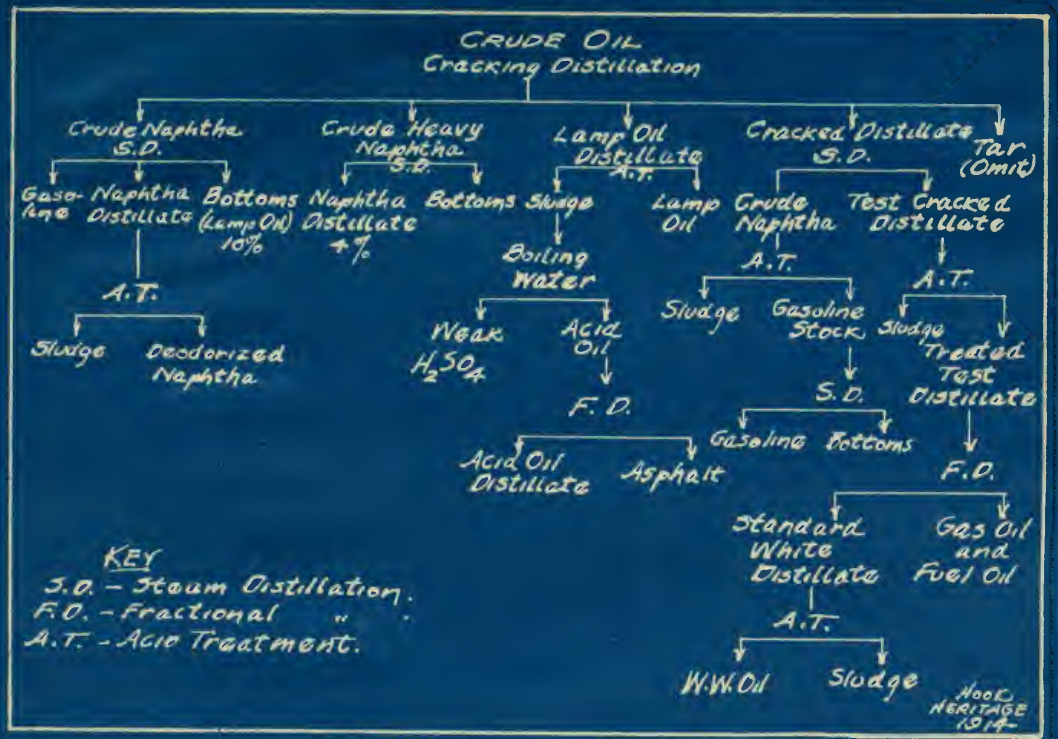
Table I.

Name.	Still Temp. Fahr.	Av. b.p. of fraction. °F.	% crude in fraction
Crude naptha.	200-325	200	7
Crude hvy naptha	325-475	300	7
Nat. lamp oil dist.	475-625	450	16
Cracked dist.	625-700	550	20

[1] Met. & Chem. Eng. XI, 389.

TABLE No II.

DIAGRAM OF PRESENT PROCESS.



It is no more than fair after quoting the above from eastern practice which consists largely of work with paraffin base petroleum to mention briefly what is said by the California State Mining Bureau on the western situation. "Many attempts have been made to convert these heavy asphaltic distillates into lighter products, either by manipulation of the original distillation or by subsequent treatment, but thus far (1904) none of the processes have met with commercial success. These petroleums are subject to cracking just as any other but owing to their chemical constitution, the light products of the decomposition have little commercial value being very foul, difficult to purify and bleach and not retaining their color when purified. The asphalt is seriously injured after cracking and the gaseous decomposition is great".(1) California petroleum contains roughly 30-40% olefins, 40-50% benzenes and napthenes, and 15-25% paraffins. Of these,

(1)Bulletin #32, March 1904, p.203.

it is seen probably 70% cannot be cracked, and this may be the key to the difficulty.

In tracing the various other methods of forcibly producing lighter fractions we find in the multitude of patents, really but five fundamentally different ideas, though many combinations of more than one. These five in the order of their appearance are: first, employment of pressure on the still and later on the condenser or both; second, the passing of the vapors through an externally heated unit between the still and the condenser; third, the use of contact or catalytic material somewhere in the system; fourth, the passage of a gas through the oil in the still with possible use of a compressor in the system; and fifth, the use of an electric current to superheat or decompose the petroleum. The authors do not claim completeness for Table III, but it was rather assembled with the view of ascertaining the trend of motor spirit production. The use of catalytic agents is especially noticeable and among these are

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Classification Of Patents — Table "III"

Country & No.	Date	Patentee	Subject	Remarks
Brit. {3345 / 1697	1865 / 1866	James Young	I	Checked Flow from Still 20" Pres
Brit. 1992	1887	Haddon	I & II	Press. 285" Settling Chamber
Brit. 10277	1889	Dewar & Redwood	I & II	Still Hd. Regulate Efflux from Cond.
Brit. 13675	1908	New Oil Ref. Process Ltd."	III	H_2O and Scrap Fe.
Brit. 376	1869	E. Meldrum	II & III	700°F. Broken Stone
Brit. 2588	1869	R. Scott	II	Heating Chamber
Brit. 50	1870	G. Shand	I	Superheated St. P=20"
Brit. 27945	1906	S.O. Coles	II	Small Tubes
Fr. 379521	1907	Wells	IV	Any Absorbent Gas
Ger. 226135	1908	Patent Hydro Carbon Ltd."	III	Fe. Filings - Air Excluded
Ger. 268176	1908	Tostelin & Renard	I. II & III	Cat. - Th. V or Al_2O_3 " - Clay
Ger. 226958	1909	—	I	Superheat to 500° C.
Brit. 16908	1909	—	III	Hydrogen. with Gyratory Motion
Brit. 23977	1909	W.A. Phillips	II & IV	" " Heating Chamber
U.S. 1004632	1910	D.T. Day	—	Hydrogenation
Brit. 28460 / Fr. 451471	1911	New Oil Ref. Pro. Ltd.	III	Oil: 3 C.M. {Fe Al_2O_3 Fec Bricks 600° / H_2O 1 Cone
U.S. 976975	1911	J.H. Adams	V	Incandescent Elect. Submerged
Brit. 3607	1912	J.H. Noad	I	
U.S. 1049667	1912	W.M. Burton	I	Temp. 340-450 F. P. in Cond. 75"
Fr. 446475	1912	C.J. Greenstreet	III	Heat with St. - Exclude Air.
Fr. 439476 / Brit 2328 1905 / Fr. 451162.	1912	L.G. Leffer	I	Use inert Gas Temp. 410 P. 11-12 At. $O + CO_2$
Brit. 25832	1912	C.W. Turner	II & III	H_2O H → Sat. Oil
U.S. 1040124	1912	E.B. Benham	V	Heats in porous mtl. Current thru Vapor
Brit. 16452	1912	C.J. Greenstreet	II & III	Oil & Steam Supplied Under Press.
Brit. 19702	1912	Flamplough	II & V	H_2O & Ni.
Brit. 20074	1912	New Oil Ref. Pro. Ltd."	III	" " + Reflux Cond.
Brit. 25631	1912	C. Ellis	I & III	P. 30-60 Heat from Comb. of Oil
Brit. 27111	1912	L. Stahn		
Fr. 452919	1913	H. Zerning	II, III & IV	Water Vapor / Gas = 1/6
U.S. 1069908	1913	E.G. Tait	IV	Natural Gas Used

I Employing Pressure on Still or Condenser or Both

II " A Heated Unit Between Still & Condenser

III " Contact or Catylitic Material or Both

IV Passing a Gas Thru Body of Oil

V Employing an Electric Current For Heat or Disso'n

Patents Taken From:

"Mineral Oils and Products" - L.J. Redwood 1897

Chemical Abstracts 1907 - 1914

found Scrap Iron, Clay, Bauxite, Coke, Brick, Al_2O_3, oxides of Th, V, Ni, Mn, Cu, etc. Water is used often and also undoubtedly plays the roll of a catalyser. In C.W.Turner's British patent #25832 of 1912, steam and oil are superheated in spirally wound tubes whereby the Oxygen of the water goes with the Carbon formed in the cracking, to produce Carbon Dioxide; and the Hydrogen is liberated and goes to saturate the unsaturated bodies, producing naptha, gasolene, etc. The water here serves not only to catalyse the reaction but takes part in it.

L. Ubbelahde[1] has studied the influence of four catalysers, Fullers earth, Kaolin, Alumina, and Nickel, and concludes that the yield of unsaturated hydrocarbons decreases with rise in temperature while the Iodine number in general increases. These two statements are hardly compatable. The nicest bit of theory however appears anonymously under the caption of "The Catalytic Production of Petrol"[1] in which

(1) Petroleum 7, 1233-38.
(2) Petroleum Review 28, 723.

a continuous flow of petroleum and hydrogen are led into the bottom of a high still. In the still is placed fine nickel and the contents are agitated. The lighter vapors are carried over by the stream of the hydrogen and the heavier condense and fall back in the still. The petroleum is thus supposed to be cracked to a saturated body and a heavier unsaturated body which is hydrogenated in the presence of the catalytic agent and is thus again cracked, again hydrogenated, and so on. Theoretically this should produce 100% gasolene.

Looking once more at Table III we see the two patentees Mr. Burke of the Independents and Mr. Burton of the Standard. The latter's process appears to be little in advance of Dewar and Redwood's of 1889, while the former has hit on the new idea of compressing the vapors while at a considerable heat and perhaps aiding a polymerization which otherwise takes place but slowly. In a recent test Mr. Burke shows a pro-

duct, 68% of which is of 0.670 gravity.[1]

In summing up the entire gasolene and motor spirit situation, Mr. B. Redwood says[2] " A fair average of the worlds production of petrol is 10%. Since the growth of demand is much greater than that of production, it is extremely unlikely that the price will fail to increase. In view of this,possible sources of motor spirits become important. These are: (1) those petroleum fractions other than the naptha fraction; (2) the products of destructive distillation of coal and shale; and (3) products of fermentation. Large quantities of petrol are now obtained from natural gas. Even petroleum wells that produce crudes containing no light fractions yield many thousands of gallons from condensable vapors. By improvement of carburettors it may be possible to use the lighter fractions of kerosene in a mixture with petrol,

[1] National Petroleum News, Vol. 5, No.5.

[2] Petroleum Review, 29, 99-100-129-130

thereby saving 20-40% petrol. An important process is the cracking of the heavier fractions where the temperature in the still is so controlled that complete decomposition is prevented. When the distillation is conducted under pressure the conversion of heavy oils to volatile ones is greatly facilitated. Cracking in contact with Iron and vaporized water produces an excellent motor spirit. Attempts to use the catalytic action of Nickel to bring about a combination with Hydrogen have been made. Such processes are destined to add greatly to the supply of petrol. Distillation and redistillation of coal tar above 800° furnishes 50,000 gallons per year of benzene and toluene but such tar cannot be profitably cracked. Alcohol is a motor spirit that can be continuously manufactured in any required quantity and a proper engine and carburettor seems destined to be the solution of the motor spirit problem.

II.

LABORATORY WORK.

General.

It was manifestly impossible to treat the whole subject of pyrogenetic decomposition of petroleum as reviewed in the preceeding pages in many times the time available for laboratory work. The authors therefore decided inasmuch as no thesis work of this nature had been carried through at the Armour Institute of Technology previously, to confine themselves to a study of the simple cracking phenomenon occuring in the still itself, to the conditions necessary for the best results under atmospheric pressure, and to testing all the types of stills available. That this present work may then be the basis of future studies, is the desire of the authors.

Two petroleums were available and three types of stills, together with a reflux still; and the mode of attack was simply to perform distillations with the various petroleums in the

various stills, varying the speed of heating and degree of heat as much as possible and redistilling the products thus obtained, analytically into fractions which could in turn be tested for refractive index, specific gravity, color and odor, stability, unsaturation, etc.

The laboratory work was carried out with a reasonable amount of care but no fine accuracy is claimed for the results. The thermometers used were taken as reading correct, for the errors in taking the temperatures on the various fractions were no doubt in excess of any calibration errors.

APPARATUS.

The Westphal balance was used to determine all gravities. These were taken at $20^{\circ}C \pm 2.5^{\circ}$ and were read usually to five units in the fourth place. Corrections for temperature were made as follows:[1]

Temp.	Gravities.		
	0.750	0.820	0.890
17.50	-.0019	-.0017	-.0016
18.75	-.0010	-.0009	-.0008
21.25	.0009	.0008	.0008
22.50	.0019	.0017	.0016

[1] Technology of Petroleum, Neubarger and Noalhat, 1901.

The refractive index was read off directly on a C. Zeiss instrument. The indices were all taken for the same run at about the same time so that temperature corrections were eliminated as much as possible. This work was also done mainly during the forenoons when the temperature was almost constant at 22°. The instrument was tested against pure distilled water and found to be practically correct.

The first reflux condenser which was used, is shown in Plate I and consisted of a still of brass of 1/8 inch thickness, about 10 inches in diameter by 10 inches high. The cap on top, brazed to the body, contained the outlet two inches in diameter, which formed the female side of a union. The male side of the union served as the bottom of the column shown in the plate. This column was 15 inches high and three inches in diameter and was supposed to serve as the main condensing surface. It terminated at the top in two tapering tubes, one leading at a slight

PLATE I

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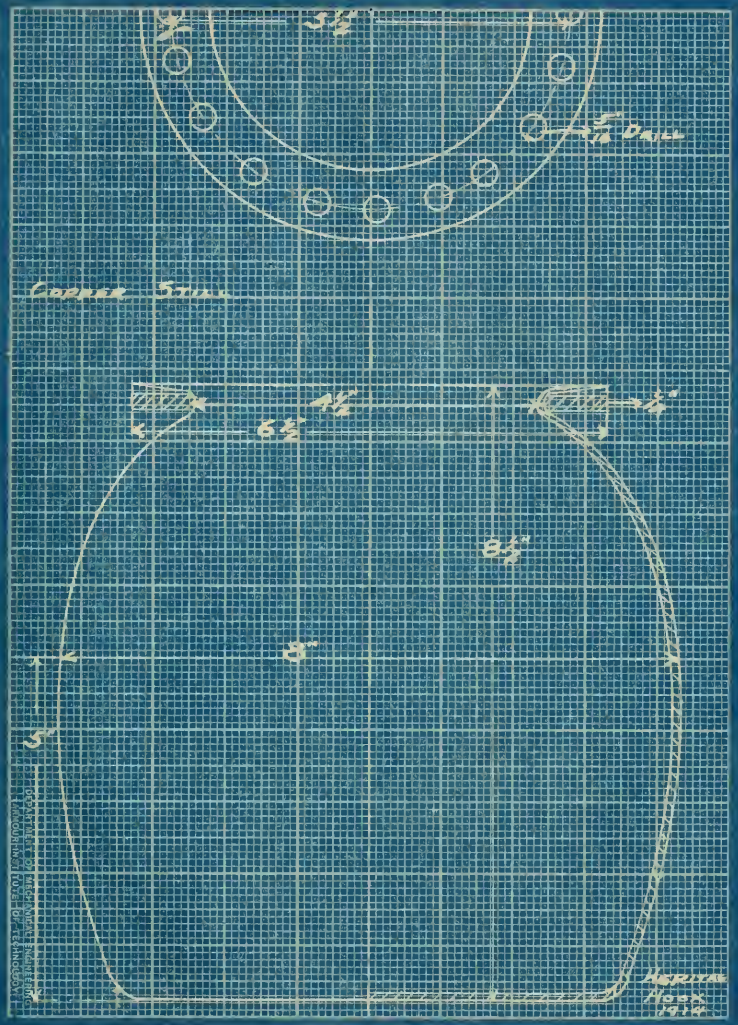
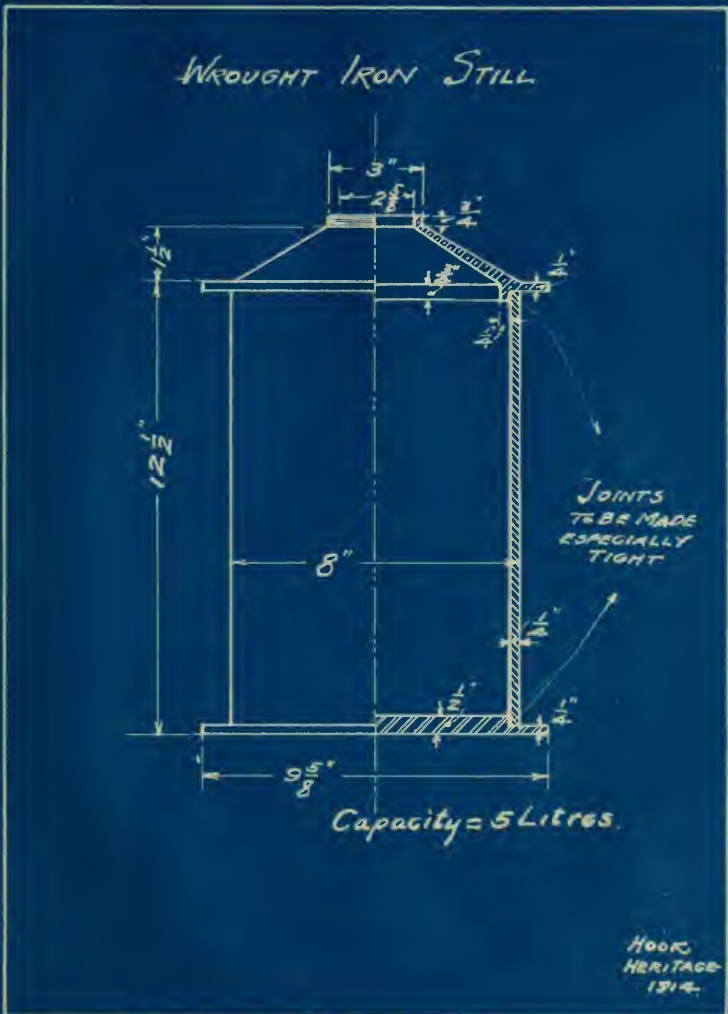
angle to the horizontal upward to a brass condenser, and the other at the same angle downward to a similar condenser. A small oil cup served to hold the thermometer at the top of the column. The design of the still was such that any amount of the more volatile products of the petroleum could be distilled off via the lower condenser, and then this could be plugged and without any transfer of the liquid, the material could be subjected to a reflux distillation. When this had been carried as far as desired the lower condenser could again be opened and the products distilled off. Thus in one still were combined all the necessary means for the study of the condition and products of the destructive distillation.

Owing to the fact that the above apparatus was put together above the union which joined the column to the still, with ordinary solder, it soon gave way under the heat to which it was necessary to subject the apparatus. This was

DRAWING 1



DRAWING No 2


WROUGHT IRON STILL
3"
2 5/8"
3/4"
1/2"
1/4"
12 1/2"
8"
JOINTS TO BE MADE ESPECIALLY TIGHT
9 5/8"
Capacity = 5 Litres.
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DRAWING 3

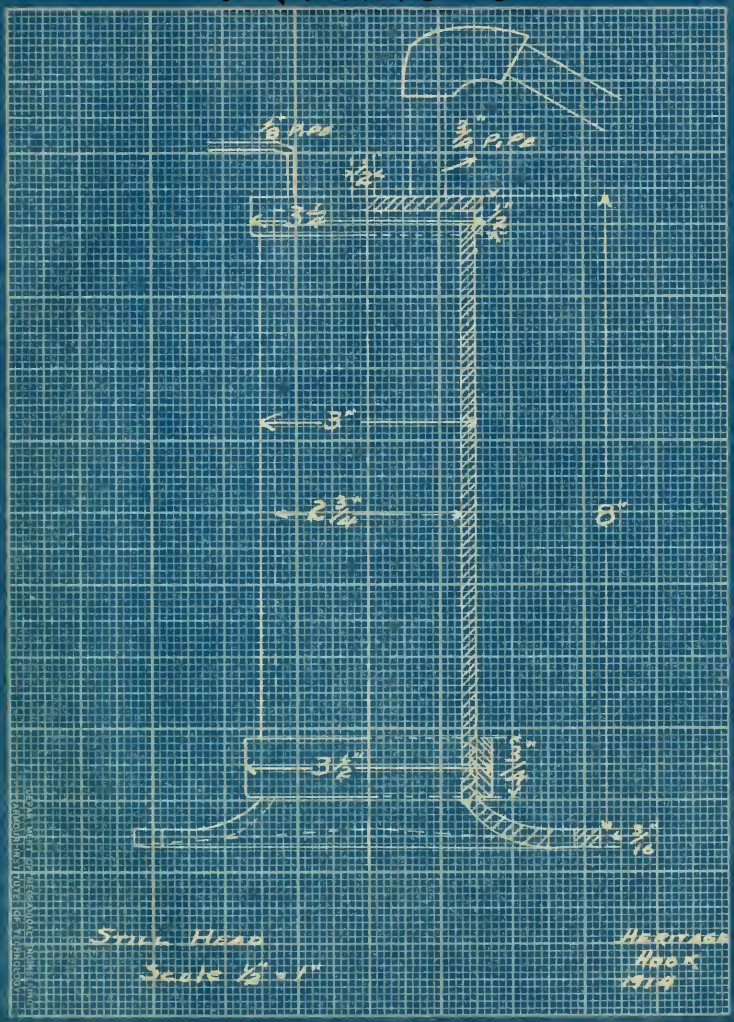

PLATE II

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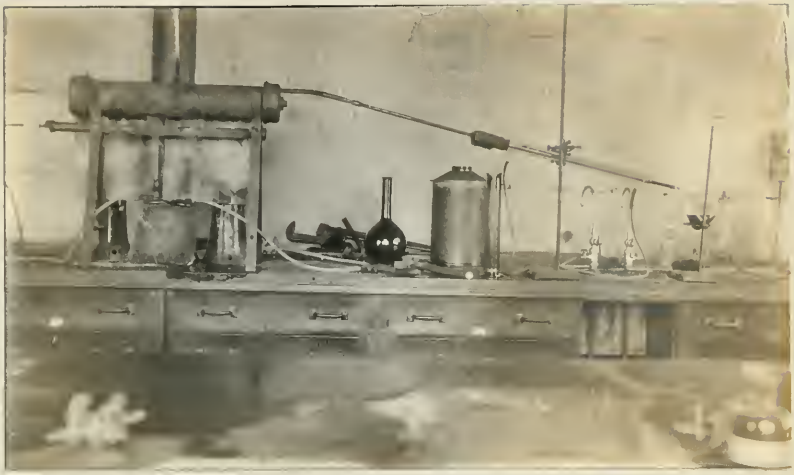
PLATE III



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1914

much to be lamented as there is no doubt but that some very interesting results could have been obtained. In the short time remaining a make shift column shown in Plate II was made of practically the same dimensions as the former and fitting the same still and upper condenser. The lower delivery pipe was however eliminated which took from the apparatus its most important point and the work with this column was far from satisfactory.

Plate III shows the still which was used for analytical purposes and was made with the view of eliminating all decomposition during the course of the distillation and securing simple fractionation of products as they were when put into the still. This was accomplished nicely especially when the distillation was made in a short space of time. All analytical fractions were obtained by coming up to the noted temperature twice. The $\frac{1}{2}$-inch pipe leading from the still served as an air condenser for about two feet before entering the water condenser.

PLATE IV

HOOK
HERITAGE
1914

PLATE V

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HERITAGE
1914

The above still was made from a 6-inch wrot iron pipe, two feet long, by closing the ends with caps and tapping one cap for a $1\frac{1}{2}$-inch plug to serve as a filling orifice and a $\frac{1}{2}$-inch hole to take the vapor pipe.

Plate IV shows the two types of stills used, the smaller one being shown in Drawing I and the larger in Drawing II. A further description of these is unnecessary except to state that the head of the small copper still was fastened to the still proper by 18 5/8-inch stud bolts, the joint being made tight by asbestos sheet packing. In the case of the large still, the head shown in the top view at the extreme right of Plate IV was screwed on, the threads being as carefully turned as possible to prevent any play in the joint.

The enlarged still head, to test which this thesis was originally proposed, appears in Plate V, screwed in place on top of one of the large stills. A working drawing of it also appears

as Drawing III. At the time this drawing was made, it was used in connection with the small stills and hence is shown coupled to a small still head. The Plate, made later after all the small stills had burned out, shows the coupling turned out and tapped to fit the newer large stills.

In discussing the stills used it should be said, that the connections were always sources of considerable trouble in preventing leakage. With this mechanical leakage going on it was of course impossible to arrive at any figures as to the loss inherent in the cracking process itself, as gas and coke.

The large stills, obtained after the small copper ones leaked so badly about the bolted joint as to be useless, were constructed wrong. Instead of being one piece of cast steel as intended, the bottoms were machined out of cast steel and then threaded so that they screwed into the wrot iron pipe serving as the still

sides. There was thus a joint of two different materials with two different coefficients of expansion and although remaining oil tight in most cases during the first heat, upon cooling the bottom sprung away from the sides in every case (four stills of this type were tested) so that the leak thus developed rendered the apparatus useless for further work. The projecting flange on bottom and top will also be noted in the working drawing. Over this was fitted a tight galvanized iron casing which was supposed to serve as an insulating cover to retain the heat and keep the upper part of the still walls hot. Instead it was found to do the opposite so that it was almost impossible to get the upper part of the still up to the required temperature. This was due also in part to the great bulk of metal used in building the still for instead of keeping the thickness of the bottom and the top down to a minimum as would have been the case had the stills been

cast in one piece, it was of course necessary to increase the thickness to get anything like an efficient joint. This bulk of metal also made any temperature control almost out of the question. The galvanized metal cylinders mentioned above were removed entirely, before using the stills.

These points in still design and the troubles encountered are here enumerated because they are considered as rather important results of the work and should be carefully considered in any subsequent work along those lines.

ANALYTICAL.

Early in the operation of the stills, it became necessary to know the amount of cracking which was taking place; and the chemical property which would tell the most in regard to this was the unsaturation of the fractions. The first work on unsaturation was carried out with sulphuric acid, upon the addition of which, a

PLATE VI

HOOK
HERITAGE
1914

dark reddish brown viscous precipitate was thrown down, this precipitate being practically the same as the sludge of the refineries. Tumski[1] says that the tars dissolve in the acid while the aromatic and unsaturated compounds form sulpho-acids with evolution of SO_2. In the olefines (C_nH_{2n}), SO_2 is said by S. F. Peckham[2] to replace two atoms of Hydrogen and these being free, unite with the free oxygen atom from the acid to form water. F. C. Robinson[3] differentiates between the action of fuming sulphuric and the concentrated sulphuric claiming that the latter takes out only the unsaturated compounds and the odiferous sulphur derivatives, while the former also attacks the aromatic series.including napthalene and anthracene. The authors therefore confined themselves to the use of the concentrated acid. (1.84).

(1) Technology of Naptha, p.204.

(2) Petroleum Report, Census of U.S. 1880

(3) Met. and Chem. Eng. XI, 389.

The nature of the sludge is a qualitative test in itself as to the compounds reacting as follows:-

(1) Paraffins and Saturated Napthas--no reaction.

(2) Olefins--a reddish brown syrupy liquid.

(3) Unsaturated Napthenes--a red-brown precipitate soluble in water.

(4) Aromatic hydrocarbons except as noted below--a red precipitate insoluble in water.

(4a) Napthalene-- a dark green precipitate.

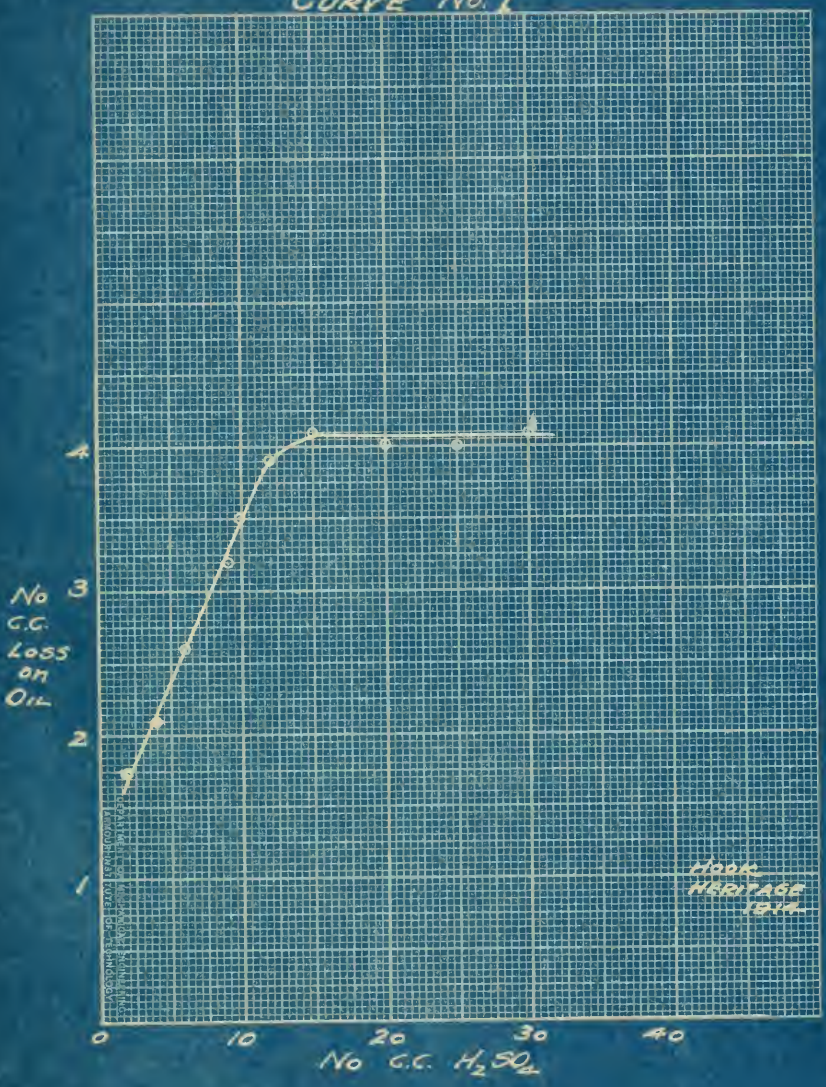
(4b) Anthracene-- a yellowish precipitate.

All sludges encountered in this work except those of the crude petroleum itself were of Class two which further supports the statement that the concentrated acid was sufficient.

The problem was now to work this sludge test into a speedy quantitative estimation of unsaturation. It had previously been used in the laboratory of the Armour Institute of Technology as a qualitative indication of the degree of purification to which an oil had been subject-

ed and was carried out by adding 5-8% acid to 100cc. of oil and after shaking, reading off the volume of oil lost. Inasmuch as one hundred cubic centimeters would mean all of many of the fractions available and often more than was available, forty cubic centimeters were first used with three cubic centimeters of acid, the mixture shaken well and allowed to stand. The quantities used were soon further reduced to 20cc. oil and 4cc. acid. It was at once noted however that check results could not be obtained, one analysis giving a loss on three portions of the same fraction as 1.3, 1.7, and 1.1cc. respectively, on 20cc. used. It remained to ascertain whether the trouble was due to different rates of settling, to insufficient mixing, or to insufficient acid. A time test was therefore made upon two fractions, Fraction #11 which had a gravity of 0.816, and Fraction #26 with a gravity of 0.821, both redistillation products. The table shows that after two hours the readings

Curve No. 1


No C.C. Loss on Oil
4
3
2
1
0
10
20
30
40
No C.C. H_2SO_4
Hook Heritage Test

become constant.

At the same time these readings were being made, five samples from Fraction #35 were centrifuged and the results again proved not to check:-

#1 --3.3 loss in 20 cc.
#2 --4.4 " " " ".
#3 --3.5 " " " ".
#4 --4.0 " " " ".
#5 --3.8 " " " ".

The mixing was also found to have no bearing on the results provided the agitation was thorough for over a minute.

The amount of sulphuric acid was now increased and the results are as shown in Curve #1. We see that the results check after the percent acid has reached 75 (15 cc. acid added to 20cc. oil) and therefore to be on the safe side the quantities for the sludge test were made 10 cc. of acid to 10cc. of distillate. This was found to give checks within 0.5% and of course could be made much more refined by using larger quantities of the materials. In order to get results speedily, the centrifuge was used and thus the

entire determination scarcely occupied ten minutes. Heavier tubes than mere graduated test tubes had to be used to withstand the centrifuging; and old burettes cut in two and each part sealed at one end served this purpose well. The loss on 10 cc. was figured to 100 cc. and termed the sludge number, since it had no actual, but merely a relative value.

The authors claim originality for the above sludge number method though in later library work the article of Day and Gilpin[1] was found. They also used equal volumes of oil and acid and shook for thirty minutes, when the sludge was drawn off, the oil washed with water, sodium hydroxide and water and after standing over night, the loss was read. The authors method though perhaps not as accurate as Day and Gilpin's, is decidedly more speedy, which was very desirable in the case of the present work.

Simultaneously with the working out of the

(1) Ind. and Eng. Chem. Vol. I, 453.

sludge number method, other methods were sought for in the literature, which would be fast and reasonably accurate. One[1] was based on matching the color of the sludge formed, --by adding 1.73 sulphuric acid, -- with standard solutions of Bismarck Brown; a second on the heat of bromination[2]; a third on the formolitic index[3]; and a fourth on Bromination with var ious complementary solutions: viz: turpentine[4], Betanapthol[5], and sodium thiosulphate[6].

Of the first it may be said that matching of sludge colors would certainly be delicate work. The heat of bromination was not attempted; and the method of obtaining the formolitic index appeared too long and complicated with no assurance of accuracy. Schmitz in Petroleum,7,239

(1) Jour. Soc. Chem. Ind. Vol.15,p.678.
(2) Jour. Amer. Chem.Soc. XVIII 378;ibid.XXI,27.
(3) Seventh Int. Cong. App. Chem,1909 Sect. IV, A.I. 9-13.
Jour. Soc. Chem. Ind. 23,p.1082;30,201,943.
Petroleum 7,239; 6,197; 6,2245-6
(4) Jour. Soc. Chem. Ind. Vol.II p.435.
(5) Oils, Fat, and Waxes, Lewkowitsch,I,393.
(6) Jour. Soc. Chem.Ind. Mills and Snodgrass 1883-435; 1884-366.
Organic Analysis--Allen Vol.III, p.4,5.

says that the amount of formolit precipitated depends on the temperature and the amount of agitation. His procedure was to add 50 cc. of sulphuric acid (1.84) drop by drop in the course of two and one half hours, to a mixture of 50 cc. oil and 25 cc. formaldehyde kept at zero degrees and constantly agitated. The excess acid is then neutralized with ammonia, the precipitate collected, washed, dried at 105° and weighed. The index is figured as the weight of formolit to 100 grams of oil and is a measure of the unsaturation.

This procedure was run through in a qualitative manner by the authors and the "formolit" product obtained, but to make any large number of estimations by this method was certainly not feasible.

There remained to be tried the various bromination methods. Allen's method is briefly as follows: A decinormal solution of Promine is made by adding 2 cc. to 750 cc carbon bisulphide. 0.3 to 1.0 gram of oil is taken, usually in carbon

bisulphide solution, and diluted to about 25 cc. with carbon bisulphide. 25 cc of Bromine solution is added whereupon the solution should be distinctly red and remain so. The flask is stoppered, agitated and placed in the dark for fifteen minutes. At the end of this period an excess of an aqueous solution of potassium iodide is poured in and after agitation, the excess of iodine is titrated with a decinormal solution of thiosulphate. The value of the bromine solution is found by running a blank. Allen notes the following precautions: first, the bromination must be carried out in the dark; second, fifteen minutes must not be exceeded as addition soon is superceded by substitution and bromine is then used up as hydrobromic acid; third, moisture must be absent as this catalyses the formation of hydrogen bromide; fourth, the volume of bromine solution should be twice that absorbed; and fifth, the oil solution should be three times the bromine solution added. If

then we take ten cubic centimeters as an average absorption on a 0.2 cc sample (a small amount) then according to Allen, it is necessary to add not less than 20 cc. of bromine solution and the volume of oil solution should be 60 cc. as a minimum. The total volume for each estimation is then 80 cc. and for seventy five estimations, this would amount to some seven liters of carbon bisulphide. It was evident at once then that the amount given above would have to be revised downward. Not knowing anything in regard to the unsaturation of the oils at hand, 1 cc. was first used as a sample, diluted to 25 cc with carbon bisulphide, and brominated with 25 cc of bromine solution. No permanent end point could be obtained, the advance being about 2 cc decinormal thiosulphate per day.

The Cailletet turpentine method was next tried except that carbon bisulphide was used as the solvent instead of alcohol for alcohol is easily oxidizable by bromine and a large error

would thus be introduced. The turpentine solution was made up, as per instructions, 4cc. in 250cc. Assuming turpentine to be mainly pinene ($C_{10}H_{16}$) with a gravity of 0.86 and that the pinene molecule adds four atoms of bromine, the turpentine solution is a little over 1/25 normal or 0.0014 grams per cc. The bromine solution later standardized against thiosulphate was 0.0035 grams per cc. The ratio between turpentine and bromine was 1cc. bromine $\equiv$0.66cc turpentine. Therefore 0.0035 should be equal to 4(0.66x0.0014) which is very nearly true. These turpentine titrations were made with a potassium iodide-starch solution as an external indicator. Three days after running the above ratio, the turpentine solution had deteriorated to such an extent that no end point could be secured after the addition of ten times as much turpentine as bromine. Therefore this method was abandoned though for one day's work it would probably serve very well. Several writers

suggest catching the end point of the bromination by the color of the solution itself and although it is true that the solution changes color as the last of the bromine goes, the error thus introduced would be 3 - 4%.

The beta-napthol method of Lewkowitsch was next studied and found to work nicely as all aqueous solutions and disagreeable carbon bisulphide were eliminated. The external indicator was the same as that used above. The original instructions were to dissolve 0.1 gram oil in 50 cc. of CCl_4 in a 250 cc. Erlenmeyer and add in excess a decinormal bromine solution in CCl_4. After fifteen minutes titrate back with an equivalent solution of beta-napthol in carbon tetrachloride. This latter is not only more pleasant to work with than the carbon bisulphide but there is no danger of bromine being lost as CS_2Br_4. Inasmuch as the supply of tetrachloride was limited, the above was modified by pipetting 0.5 cc of the fraction to be brominated

into a small bottle and adding 25 cc of tetrachloride. Ten cubic centimeters of this solution was then brominated by adding from 15 to 25 cc. bromine as the unsaturation of the sample demanded. This left 15 cc of the oil solution for a duplicate determination, should anything go wrong with the first one.

The product formed when beta-napthol and bromine react is supposed to be a mono-bromnapthol. The amount of beta-napthol per cc was determined by slowly evaporating the tetrachloride from 5 cc of the solution and weighing the residue. An average of three determinations was 0.007 grams per cc.

$C_{10}H_7OH \equiv Br.$ 1 cc beta-napthol ≡ 1.34 cc bromine.

Therefore: 1 cc Br. $= \frac{0.007 \times 80}{144 \times 1.34} = 0.0029$ grams per cc.

Subsequent standardization as noted above with thiosulphate gave 0.0034 grams bromine per cc.

This method was found to give good results in minimum time with duplicates often checking exactly.

Somewhat later the authors returned to the thiosulphate method and found wherein the previous trouble of the flitting end point lay. By using the small sample of 0.2 cc oil and by adding a large bulk of water immediately on removing the flask from the dark and then using a good excess of saturated potassium iodide solution with reasonable rapid titration the end point was sufficiently permanent to be practicable. This method was then used on Runs #8 and #9 toward the end of the work.

It was necessary then to determine whether the two methods gave comparable results and to this end three separate fractions were brominated both ways with the following result:

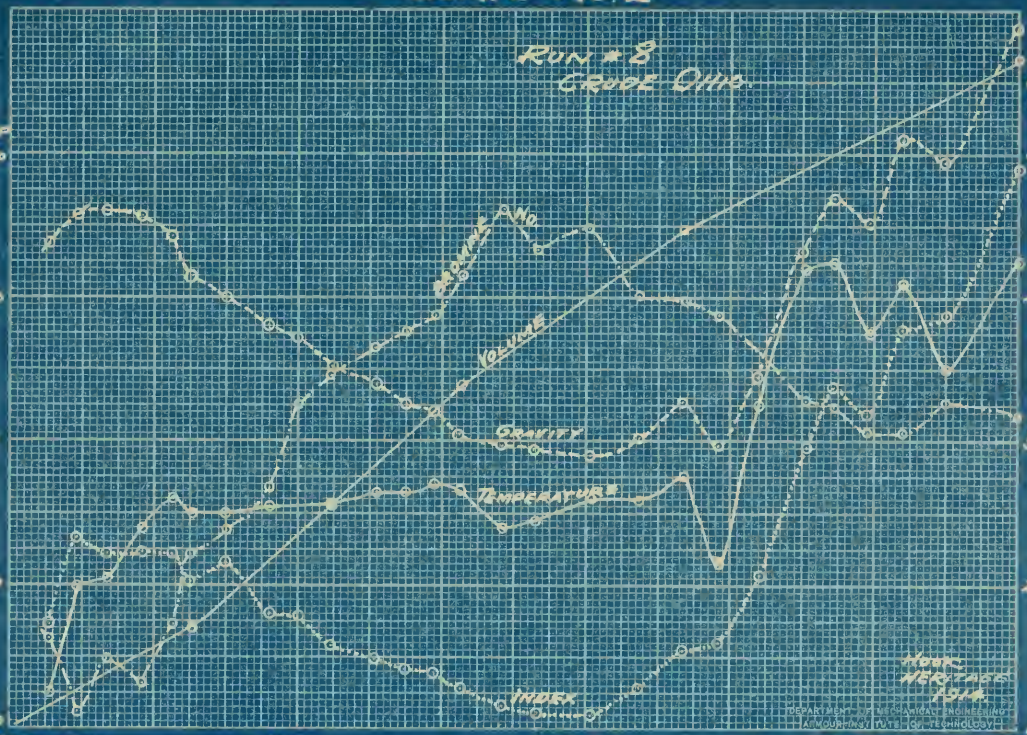
Fraction No.	Bromination Number.	
	With Beta-napthol.	With $Na_2S_2O_3$
41	54.0	52.5
40	78.2	77.3
38	36.4	36.3

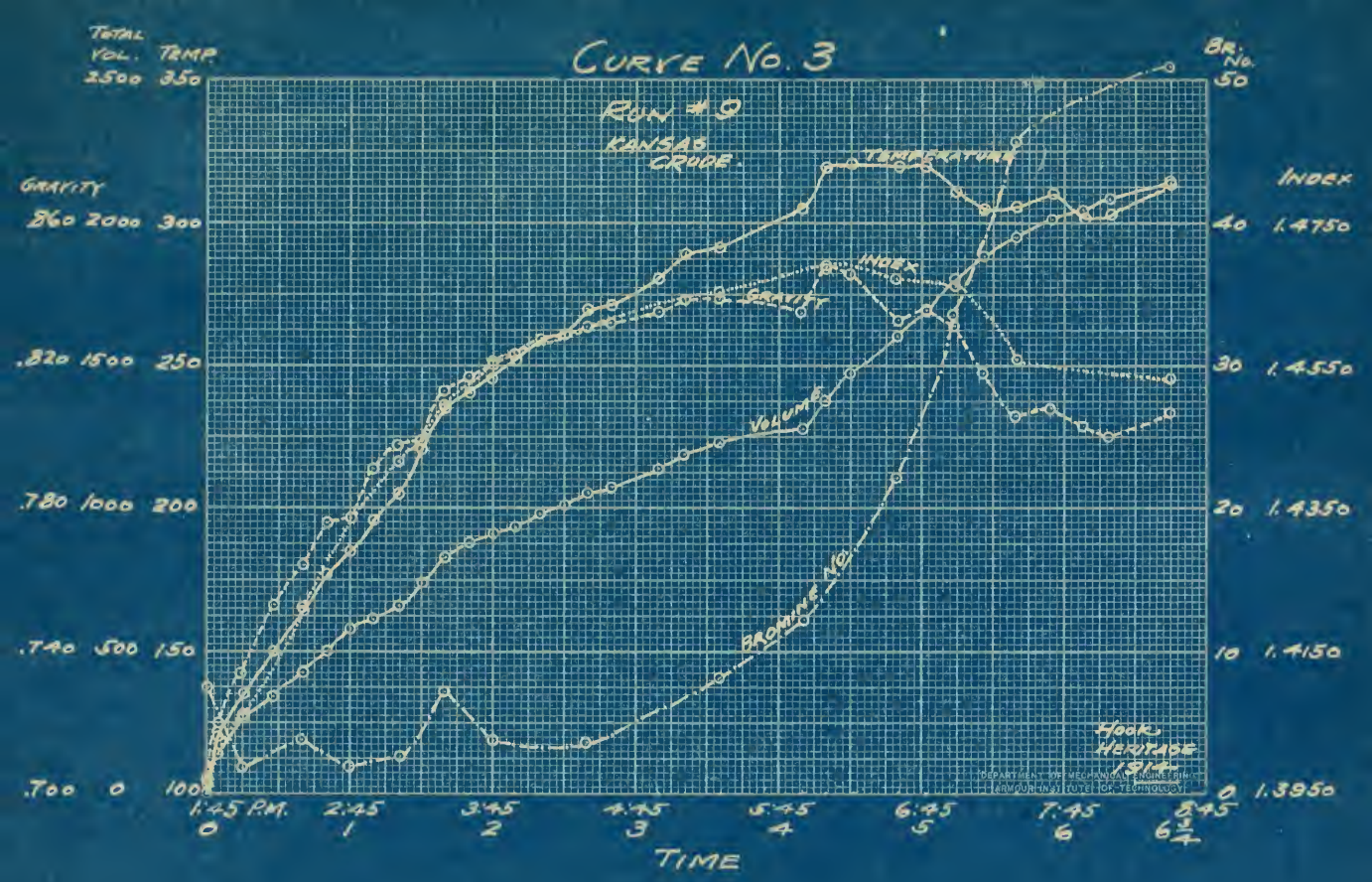
The computation in figuring the bromination

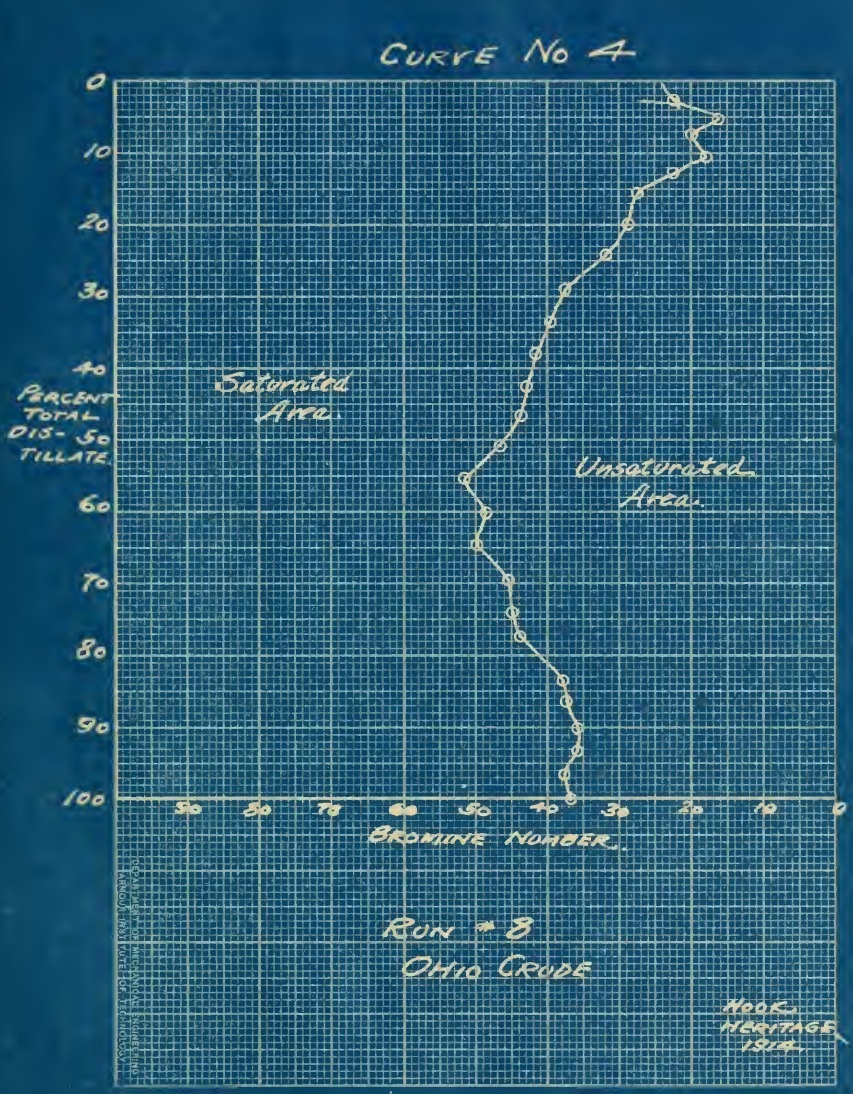
number, which is also simply a relative number and not absolute, may be stated thus: $100 \frac{n\ b}{.2g}$= bromination number, where n is the number of cubic centimeters of bromine used, b is the bromine standard, and g the gravity of the fraction. Where the bromine solution is used over and over for days it may be further simplified to $\frac{k\ n}{g}$= number.

A comparison of the two acceptable methods, viz: sludge number and bromine number, was made with the hope of finding a constant ratio between them. Table V gives these results, and it will be noted that though the majority of the ratios fall around three, this figure is not sufficiently constant to be of anything like a quantitative nature. The ratio falls considerably in the two cases marked Run #5 and Run #7 due no doubt to the fact that these products had not been distilled and the tarry products remaining in the oil made an abnormal sludge number.

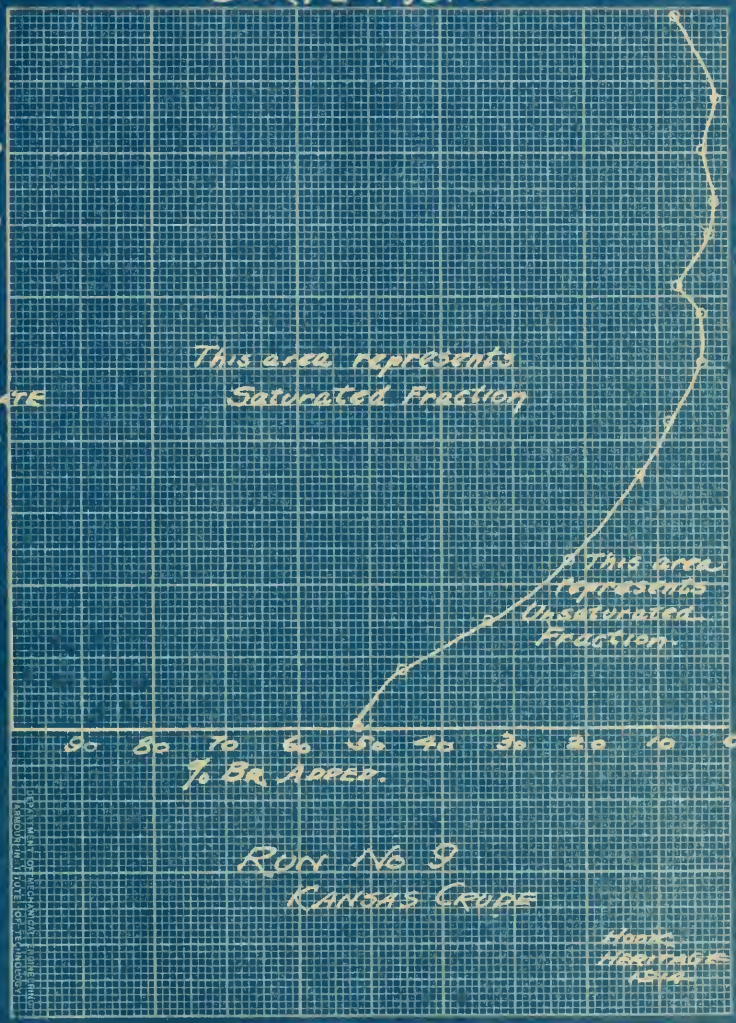
CURVE NO. 2


RUN # 8
CRUDE OIL
PRESSURE
VOLUME
GRAVITY
TEMPERATURE
INDEX
HOURS
TOTAL VOL. 2700
GRAVITY .860 .840 .820 .800
TEMP 200° 160° 100° 50°
BR. NO. INDEX 55 45 35 25 15
1.4950 1.4850 1.4750 1.4650 1.4550
0 260
10:00 A.M. 11:00 NOON 1:00 P.M. 1:30
1 2 3 3½
TIME.
DEPARTMENT OF CHEMICAL ENGINEERING
ARMOUR INSTITUTE OF TECHNOLOGY


CURVE NO. 3
RUN #9
KANSAS CRUDE.
TEMPERATURE
INDEX
GRAVITY
VOLUME
BROMINE NO.
HOOK NEEDLE STYLE
TOTAL VOL.
TEMP.
BR. No.
GRAVITY
INDEX
2500 350
.860 2000 300
.820 1500 250
.780 1000 200
.740 500 150
.700 0 100
50
40 1.4750
30 1.4550
20 1.4350
10 1.4150
0 1.3950
1:45 P.M. 2:45 3:45 4:45 5:45 6:45 7:45 8:45
0 1 2 3 4 5 6 6 1/4
TIME
DEPARTMENT OF MECHANICAL ENGINEERING
ARMOUR INSTITUTE OF TECHNOLOGY


CURVE No 4
0
10
20
30
40
PERCENT TOTAL DIS- TILLATE.
50
60
70
80
90
100
Saturated Area.
Unsaturated Area.
90
80
70
60
50
40
30
20
10
0
BROMINE NUMBER.
RUN # 8
OHIO CRUDE
HOOK HERITAGE 1924

Curve No. 5



Run No. 9

Kansas Crude

DISTILLATIONS.

Two petroleums were used in the various distillations, representing quite different types of crude. The one used on all the preliminary work, in fact all the runs except the last, was an extremely heavy dark green petroleum from Ohio. The last run was made on a rather light crude from Kansas, purchased from the Standard Oil Co. Analyses of these petroleums appear as Table VI.

A satisfactory tabulation of the runs is hard to get and it was thought best to submit them in two ways, first as in Tables VII to X inclusive according to runs, and second, as in Tables XI and XII according to "Distillation" and "Redistillation". It was found at once that redistillations were necessary to separate the products of the first cracking and hence every "run" consists of a distillation and one to three redistillations.

The cracking temperature was found to be

in the neighborhood of 300° C. varying either way 20 degrees according to the size and nature of the charge being cracked. As the cracking progressed the temperature would rise for a certain time and as the decomposition point was reached would drop quickly, sometimes twenty degrees or more, and then build up again. It was proved by work with the reflux still that an oil cannot be cracked in this manner as long as the boiling point of the whole mass of liquid is below 275° C. This is shown by the analytical distillation of all of fraction #45 after reflux boiling, appearing in Table X; also the data tabulated in Table XIII although the Ohio oil did suffer some reduction in gravity inasmuch as it was such a heavy petroleum. This brings up the point, --which is simply another way of stating the above--, that the heavier the petroleum the easier it is to crack. The summary of the whole business is then, that the lighter portions must be distilled off before cracking can be

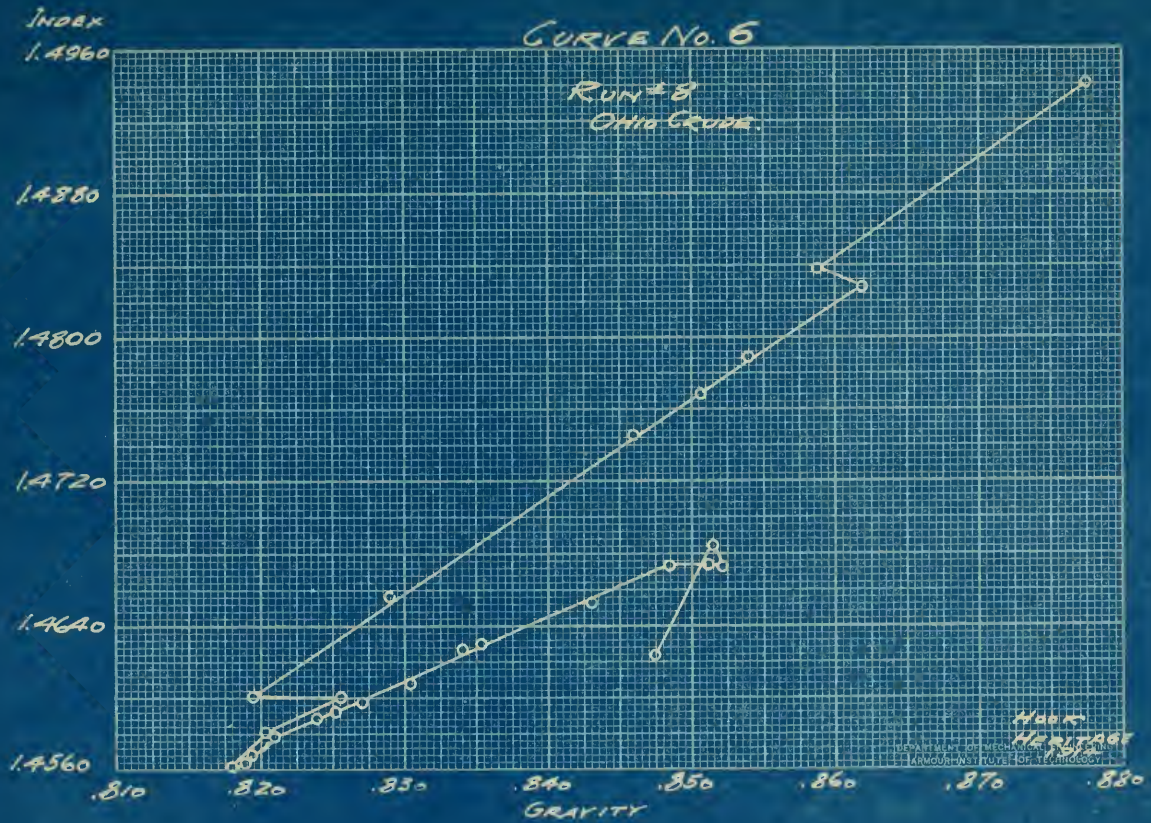
induced, that it proceeds at a certain temperature destroying an intermediate fraction of the petroleum along about the lubricating gravity and leaving much lighter and much heavier portions which do not yield readily if at all to further decomposition. Reference to the second redistillations in the various tables proves that practically all the decomposition takes place in the first distillation and succeeding redistillations even in the cracking stills do not further break up the heavy fractions.

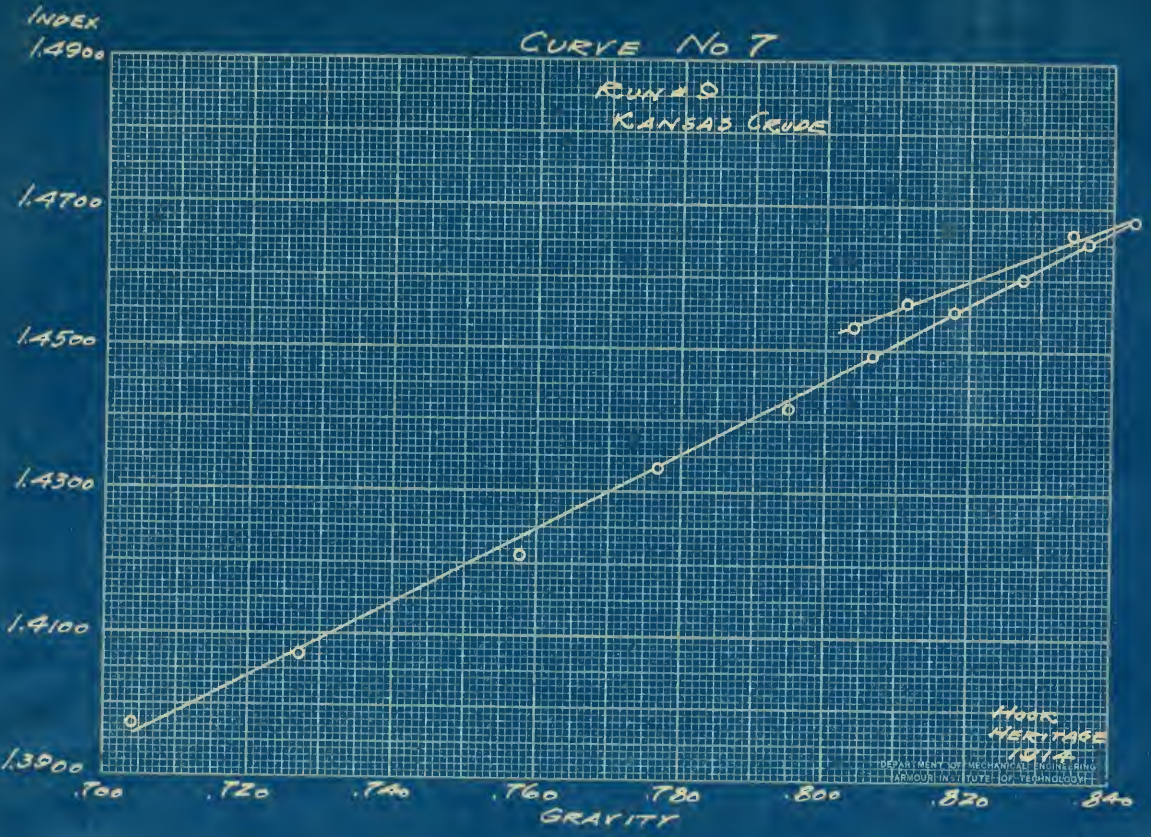
Both the copper stills with enlarged head and the wrought iron stills proved efficient though which was the more so could hardly be ascertained, due to mechanical leaks and to the difference in capacity between the two types. The lowest gravity fraction (#44) was produced from the Ohio oil in the wrought iron still with enlarged head. The enlarged head on this type however made little difference as the still itself was tall and difficult to heat.

Attention is called to the fact that the distillations carried out in the longest time

produced the lightest fractions although not necessarily the greatest per cent of volume charged. The total time in which the distillation was made perhaps has not so much bearing on the products as the fraction of the total time consumed between each temperature. All these variables are included in the tables and an almost endless discussion of the results could be entered into, and a great number of curves plotted of each variable against some other. The value of many of these would no doubt be questionable and hence the authors leave the close perusal of the data tables to the readers' inclinations.

An additional word should be said in regard to the color and odor of the distillates. Discoloration, especially with time, and bad odor became worse with the fractions of higher boiling point, and not necessarily with those of high unsaturation as would be expected. None of the distillates were purified according to the regular program of the refineries, which


INDEX
CURVE No. 6
1.4960
1.4880
1.4800
1.4720
1.4640
1.4560
RUN # 8
Ohio Crude.
.810
.820
.830
.840
.850
.860
.870
.880
GRAVITY
HOOT
HERITAGE
DEPARTMENT OF MECHANICAL ENGINEERING
ARMOUR INSTITUTE OF TECHNOLOGY


CURVE No 7
RUN # 9
KANSAS CRUDE
INDEX
1.4900
1.4700
1.4500
1.4300
1.4100
1.3900
.700
.720
.740
.760
.780
.800
.820
.840
GRAVITY
HOOK
AVERAGE
CURVE
DEPARTMENT OF MECHANICAL ENGINEERING
ARMOUR INSTITUTE OF TECHNOLOGY

purification would of course make them more stable. This study would have been undertaken had time permitted.

The index of refraction was studied with a view to ascertaining the effect of unsaturation on this property. C. Ellis[1] says that with vegetable oils on the addition of Hydrogen or, --which is the same thing--, on the increase in saturation, the index falls. We would therefore expect that as the mineral fractions become more unsaturated the index would rise. A study of the data of Runs 8 and 9 proves this beyond a doubt. Curves 6 and 7 show that as the index is plotted against the gravity, which latter is really the main factor in the index change, when that part of the run is reached where the cracking took place, the curve changes grade and assumes a higher position. This can be explained in no other way than as noted above. It was attempted to form-

[1] Jour. Ind. and Eng. Chem. Vol 6,p.117

ulate an empirical rule governing this increase but without success, although it may be seen from the curves that the ratio is practically constant.

It is needless to further discuss the results as the curves are self explanatory. Curve #2 may be noted as especially good in bringing out sharply the cracking period with the various changes induced by the phenomenon in the divers variables.

COMMERCIAL MOTOR SPIRITS AND GASOLENE.

RUN #10.

This run consisted of a distillation of commercial gasolene in the tube still. As will be seen from the following data, the fraction was too light to draw much of a comparison between this and the crude oil distillates which have been described in the foregoing work.

One liter of the gasolene (sp.gr. 0.706 at 20^0) was charged into the still and the fractions obtained are shown in Table XVI.

RUN #11.

The essential part of this run was to determine as nearly as possible the primary constituents of motor spirits. This is a product of recent work and is put on the market by the Standard Oil Co. A visit to the plant at Whiting, Ind. made showed that the future of this product was practically settled and these people are spending a great amount of money enlarging their plant for the production of these motor spirits.

A few words concerning the distillation may be interesting. The crude charge is made up of fuel oil(sp.gr.0.870) which formerly has been sold for about 3¢ per gallon. This is charged into large cylindrical stills and a pressure of 70# is maintained and kept constant by means of check valves. The pressure is due entirely to the vapor of the oil. The distillate resulting from this, at a temperature of about 700°F., consists of light gasolene and kerosene at a sp.gr. of 0.725. This fraction is completely saturated and is redistilled in steam to further

purify it. The remaining oil is further heated in the stills until all the lubricating fraction has been removed. This lubricating oil is the only oil on the market which is heavier than water. The residue left in the stills is chiefly coke and owing to the nature of the original charge, this coke is the purest obtainable and finds a ready market.

To summarize the economic value of this product we have only to glance at the current figures from the market. A fraction, fuel oil, which has been practically worthless, being disposed of at 3¢ per gallon, has been "cracked" without any elaborate process, and the resulting fraction is now put on the market at 2¢ less per gallon than the market price of gasolene.

TABLE IV.

Time Tests on Sludge.

Fraction #11, 20 cc. oil and 4 cc. acid.

Time.	Vol. Oil	Loss.	Sludge No.
1:55	17.3	2.7	13.5
2:10	17.1	2.9	14.5
2:25	17.1	2.9	14.5
2:40	17.2	2.8	14.0
3:00	17.3	2.7	13.5
3:20	17.55	2.45	12.2
3:40	17.85	2.15	10.7
4:00	17.90	2.10	10.5
4:30	17.90	2.10	10.5
8:45	17.90	2.10	10.5

Fraction #26, 20 cc oil and 4 cc acid.

10:30	16.6	3.4	17.00
11:00	16.6	3.4	17.00
11:30	17.25	2.75	13.75
12:00	17.30	2.70	13.50
12:30	17.30	2.70	13.50
1:00	17.30	2.70	13.50

TABLE V.

Fraction	Gravity	Sludge No. loss per 100 cc.	Promine No. Addition per 100 cc.	Ratio= Promine / Sludge
		Ohio Oil		
34	.736	23.3	66.6	2.86
37	.842	9.65	32.3	3.35
38	.839	13.5	36.4	2.69
39	.871	12.0	31.5	2.63
40	.749	27.0	78.2	2.89
41	.825	20.0	54.0	2.70
42	.864	14.0	26.3	1.88
Crude	.894	13.2	9.4	2.94
Run #5	.894	31.0	15.4	* .495
Run #7	.888	17.0	18.2	* 1.07
44	.719	24.0	70.0	2.92
50	.784	17.0	58.9	3.45
52	.852	11.5	33.8	2.94
		Kansas Oil.		
53	.734	3.0	6.45	2.15
55	.815	3.0	6.80	2.27
56	.839	6.0	9.80	1.63
59	.775	16.5	60.6	3.66
60	.831	10.0	30.2	3.02

TABLE VI

ANALYSIS OF OHIO CRUDE

Viscosity at 40°F.	70
" " " 100 "	356
Flash point	305°
Burning point	375°
Sludge number	3.2
Bromine number	9.4
N	1.4816
Sp. gr.	0.894 or 26.8 Baumé.

Analytical distillation: no distillate over under 260°C. 260-300°, 4.6% Sp.gr.=0.852; Br=17.1; N=1.4675; Residue=95.4%. 1½% solid paraffin; ½% asphaltic residue.

KANSAS CRUDE.

Sp. gr. 0.853, Sl.= 2.75; Br.=8.4; N=1.4762

ANALYTICAL DISTILLATION.

No.	Temp.	Sp.gr.	Vol.	% vol.	Sl.	Br.	N
53	150	0.734	165	11.	3.0	6.45	1.4109
54	200	0.776	185	12.3	---	2.7	1.4318
55	250	0.815	220	14.7	3.2	6.8	1.4520
56	300	0.839	185	12.3	6.0	9.8	1.4658

1500cc charged; residue 725cc or 48.3%; loss 20cc or 1.3%.

TABLE VII.

RUN #1.

DISTILLATION.

Copper still Empty Enlarged head. 1420 cc.

Fraction No.	Time	%Total time.	Temp.	Sp.Gr.	Vol.	% Vol. Ch'ged.
1	4:00	27	300	.846	150	10.6
2, 3	5:05	50	328	.839	630	44.5
4	5:35	23	335	.834	360	24.9
		1st REDISTILLATION. Same Still.				
5	9:21	27	150	.734	75	6.8
6,7,8	9:40	50	300	.820	430	37.7
9	9:50	25	330	.861	230	20.6
		2nd REDISTILLATION. Same Still.				
10	1:59	53	150	.746	55	7.5
11	2:45	38	300	.838	260	35.6
12	2:55	9	325	.859	80	10.9

Distillation started 3:25, Total time 130 mins. Residue--none. Loss=280cc=20%

1st Redistillation started 9:10, Total time 40 mins. Total charge 1140; Residue--345=29.7%; Loss--60=5.2%

2nd Redistillation started 12:55, Total time 120 mins. Total charge 730; Residue --335=46%.(Loss included)

TABLE VIII.
RUN #3

DISTILLATION.

Copper Still. Empty enlarged head.

Frac No.	Time	%Tot Time	Temp.	Sp.Gr.	Vol.	%Tot. Vol.	Sl.
16	8:45	50.	300	.854	115	11.5	12.5
17	9:05	33.5	315	.853	270	27.0	11.25
18	9:15	16.5	325	.845	385	38.5	11.25

Started 8:15; Total Time--60 mins. Total charge--1000 cc.; Residue and Loss--230 cc=23.%

1st-REDISTILLATION.

19	1:38	50.	150	.744	70	9.1	15.5
20	1:45	27.	300	.833	245	32.	8.5
21	1:51	23.	340	.864	150	19.5	5.5

Started 1:25; Total time--26 mins.; Total charge--760 cc. Residue--280cc or 36.5%; Loss--20cc or 3.9%.

2nd REDISTILLATION.

22	3:33	20.	150	.752	65	8.8	14.5
23	4:05	49.	300	.824	200	27.0	10.5
24	4:25	31.	370	.862	380	51.5	7.5

Started 3:20; Total time--65 mins.; Total charge--740 cc; Residue--73cc or 10%; Loss--22cc or 3%.

3rd REDISTILLATION.

25	2:15	31.5	150	.745	66	10.2	14.0
26	2:42	45.	300	.821	235	36.4	12.0
27	2:56	23.5	376	.869	283	43.9	1.5

Started 1:56; Total time--60 mins.; Total charge--645 cc; Residue--26cc or 4%; Loss--35cc or 4.5%

TABLE IX.
RUN #4.

DISTILLATION.

Copper Still. Empty enlarged head.

Frac No.	Time	%Tot Time	Temp.	Sp.Gr.	Vol.	%Tot. Vol.	Sl.
28	12:04	78.	300	.837	170	11.4	6.75
29	12:16	5.	330	.854	425	28.5	7.50
30	12:50	17.	350	.843	715	47.5	10.75

Started 9:46; Total time 180 mins.; Total charge--1500; Residue--10cc or 1%; Loss--180 cc or 12.6%

1st REDISTILLATION.

31	10:30	26.5	150	.724	106	8.15	15.75	
32	11:44	43.5	300	.822	385	30.0	11.0	
33	12:35	30.	390	.865	620	47.5	6.5	

Started 9:45; Total time 170 mins.; Total charge--1300 cc; Residue 120 cc or 9.25%; Loss--60cc or 4.6%

2nd REDISTILLATION.

								Br.
34	9:35	34.5	150	.736	120	11.5	23.3*	66.6
35	10:23	37.	300	.826	445	42.5	20.5	----
36	11:00	28.5	375	.870	430	41.0	----	24.9

*Sludge method changed here from 20cc oil and 4 cc acid to 10cc oil and 10cc acid.

Started 8:50; Total time 130 mins.; Total charge--1045cc; Residue--25cc or 2.5%; Loss--25cc or 2.5%

TABLE X.

RUN #6.

Fraction No.	Time	%Time	Temp.	Sp.Gr.	Vol.	% Vol.	Sl.	Br.	N
37	4:26	62	300	.842	125	12.5	9.65	32.3	
38	5:02	30	330	.839	680	68.0	13.5	36.4	1.4703
39	5:10	8	340	.871	65	6.5	12.0	31.5	1.4882

Copper Still; Head full of glass rods; started 3:10; total time 120 total charge 1000; Residue--20=2%; Loss--134=13.4%

1st REDISTILLATION.

40	10:25	23	150	.749	100	11.5	27.	78.2	1.4204
41	11:20	31	300	.825	270	31.	20.	54.0	1.4672
42	12:40	46	365	.871	368	42.	14.	26.3	1.4804

Started 9:45; total time 175 mins.; total charge 870; Residue--55= 6.3%; Loss--77=8.8%

RUN #8.

ANALYTICAL DISTILLATION.

44	150	.719	142	7.0	70.0	1.4083
45a	200	.775	330	16.3	59.9	1.4359
45b	250	.835	490	24.1	41.5	1.4640
45c	300	.859	465	23.0	30.0	1.4768

Charge--2027; Residue--640=31.6%; Loss--102=5.3%.
All #45 boiled in reflux for 145 mins. Maximum temp. 185°

TABLE X CONT'D

RUN#8 Cont'd.

ANALYTICAL DISTILLATION.

Fraction No.	Time	%Time	Temp.	Sp.Gr.	Vol.	% Vol.	Sl.	Br.	N
49			150	.750	17	1.4		72.9	1.4180
50			200	.784	240	20.0		58.9	1.4387
51			250	.831	370	30.8		42.9	1.4619
52			300	.852	250	20.8		33.8	1.4718

Charge--1200; Residue--260=21.6%; Loss--60=5%.

RUN #9.

ANALYTICAL DISTILLATION FROM FRACTION #12(See Table XV)

58			150	.723	67	4.6		65.8	
59			200	.775	175	12.1		60.6	
60			250	.831	350	24.1		30.2	
61			300	.848	460	31.6		18.8	

Charge--1450 cc.; Residue and Loss--400cc or 27.6%

TABLE XI.

DISTILLATIONS.

Run No.	Total Time	% Under 300	Sludge No.	Sludge Sp.Gr.	% 300-330°	Sludge No.	Sludge Sp.Gr.
1	130	10.6	----	.846	44.5	----	.839
3	60	11.5	12.5	.854	65.5	11.25	.849
4	180	11.4	6.75	.837	28.5	7.50	.854
6	120	12.5	9.65	.842	68.0	13.50	.839

TABLE XII.

1st REDISTILLATIONS.

Run No.	Total Time	% Under 150	Sludge No.	Sludge Sp.Gr.	%150-300°	Sludge No.	Sludge Sp.Gr.
1	40	6.5	----	.734	38.	----	.820
3	26	9.1	15.5	.743	32.	8.5	.832
4	170	8.15	15.75	.724	30.	11.0	.822
6	175	11.50	*27.0	.749	31.	20.0	.825

*Revised sludge method.

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TABLE XIII.

REFLUX WORK.

RUN #2.

Charge 740cc; Time 130 mins. Max.Temp. 155°. Loss--90cc or 12%.

ANALYTICAL DISTILLATION.

Dist. No.	Temp.	Sp.Gr.	Vol.	% Vol.	Sl.	Br.
13	175	.774	40	6.2	15.0	----
14	250	.824	80	12.5	10.0	----
15	325	.861	190	29.5	3.5	37.5

Vol. charged 645 cc; Residue--285 or 44%; Loss--50cc or 7.5%; No temperature under 150°.

RUN #5.

(a) Charge--1000cc. Time 85mins. Max.Temp.220.Leaky still.
(b) " --1000cc. " 25 " . " . " .100. " "
(c) " --1000cc. "" 42 " . " . " .275.

No.	Temp.	Sp.Gr.	Vol.	% Vol.	Sl.	Br.	N_{25}
43	----	.894	915	92.5	31.	15.4	1.475

RUN #7.

Charge 1000cc; Time 105 mins.; Max. Temp. 280.

ANALYSIS OF ENTIRE RUN.

Sp.Gr.	Br.	Sludge	N_{25}
.888	18.2	17	1.471

ANALYTICAL DISTILLATION.

(about 20cc over between 150 and 250 cc.)

No.	Temp.	Sp.Gr.	Vol.	% Vol.	Br.	N
47	300	.854	360	36.	26.5	1.4716
48	Residue		480	48.	Loss of 12%	

TABLE XIV.

RUN #8.

3000cc Ohio oil, wrought iron still.

No.	Time.	Temp.	Sp. Gr.	Vol.	Br.	N
1	10:08	265	.8475	---	21.3	1.4623
2	10:14	280	.8515	---	16.2	1.4684
3	10:20	281	.852	---	19.9	1.4672
4	10:27	288	.8515	---	18.1	1.4674
5	10:33	292	.8485	---	22.3	1.4672
6	10:38	290	.843	365	27.2	1.4652
7	10:45	290	.840	---	28.8	1.4666
8	10:54	291	.836	---	31.8	1.4630
9	11:00	293	.8345	---	37.5	1.4628
10	11:07	291	.830	425	39.6	1.4608
11	11:16	293	.827	---	41.5	1.4599
12	11:22	293	.825	---	42.7	1.4592
13	11:28	294	.824	---	43.8	1.4589
14	11:33	293	.821	495	46.6	1.4579
15	11:43	288	.8195	---	51.2	1.4566
16	11:50	289	.819	---	48.4	1.4561
17	12:01	292	.818	---	49.9	1.4560
18	12:11	292	.8205	---	45.1	1.4579
19	12:19	295	.8255	542	44.9	1.4605
20	12:28	283	.8195	---	48.8	1.4610
21	12:36	305	.829	---	----	1.4657
22	12:46	324	.8465	---	37.8	1.4746
23	12:51	325	.854	---	37.4	1.4787
24	12:59	315	.8505	---	35.6	1.4768
25	1:06	322	.862	---	35.7	1.4828
26	1:15	310	.859	---	37.8	1.4838
27	1:45	325	.8775	590	36.8	1.4940

95cc Residue.

500cc Loss due to leaky still.

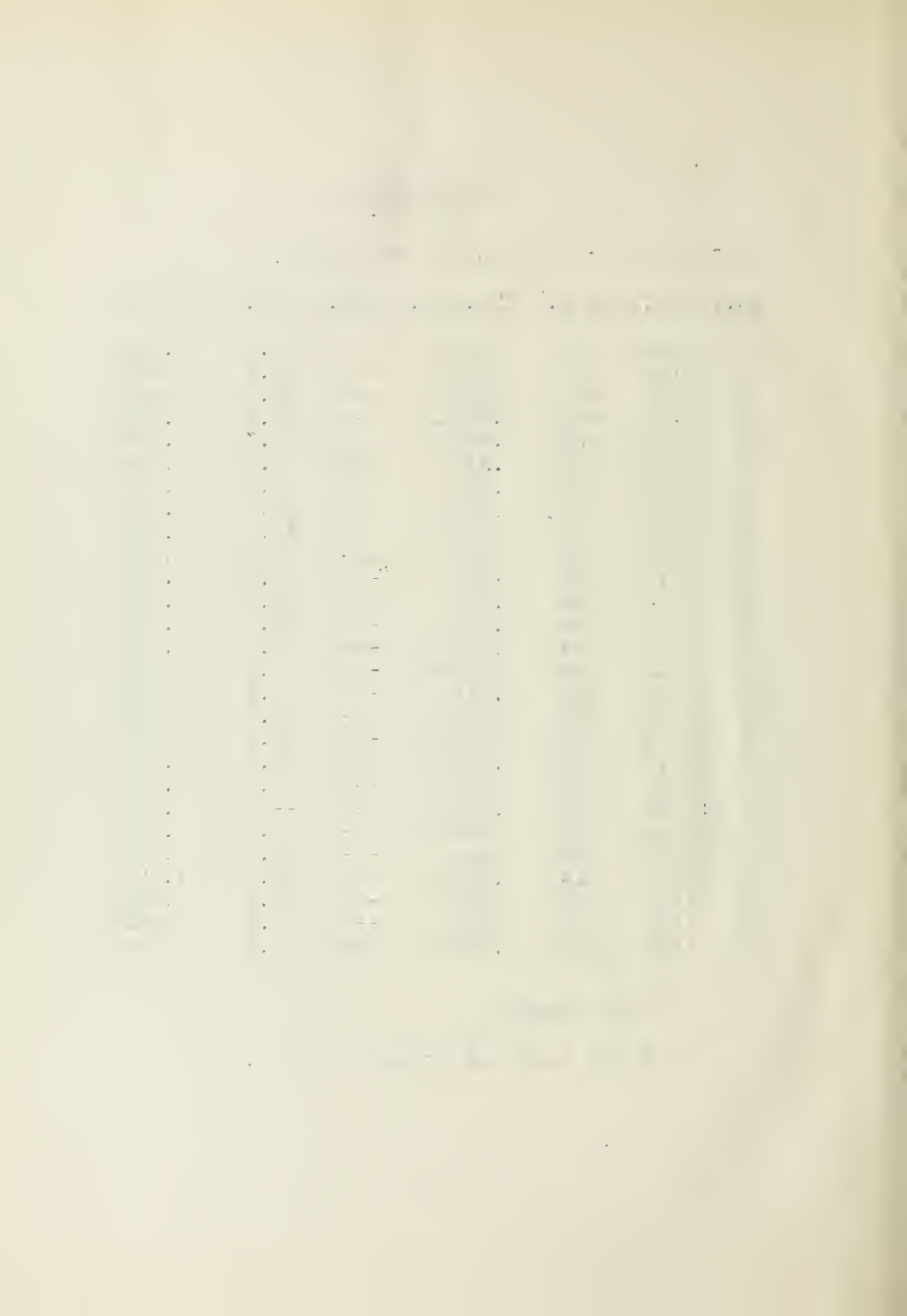

TABLE XV.
RUN #9.

3000cc. Kansas, Wrought iron still.

No.	Time.	Temp.	Sp. Gr.	Vol.	Br.	N
1	1:45	100	.704	23	7.45	1.3970
2	1:50	120	.720	120		
3	2:00	135	.734	120	1.9	1.4060
4	2:13	150	.753	82		
5	2:25	164	.764	78	3.7	1.4211
6	2:35	177	.776	78		
7	2:45	185	.777	74	2.0	1.4336
8	2:55	196	.791	40		
9	3:05	205	.798	49	2.65	1.4415
10	3:15	221	.799	74		
11	3:25	235	.813	87	7.2	1.4491
12	3:35	241	.817	52		
13	3:45	246	.820	29	3.85	1.4553
14	3:55	252	.823	24		
15	4:05	259	.826	48		
16	4:15	262	.829	32		
17	4:25	270	.831	40	3.60	1.4601
18	4:35	272	.832	26		
19	4:55	282	.835	61		
20	5:05	289	.839	50		
21	5:20	292	.839	40	8.20	1.4651
22	5:55	305	.835	50		
23	6:05	319	.848	106	12.20	1.4688
24	6:15	321	.846	92		
25	6:35	320	.833	130	22,10	1.4672
26	6:47	320	.836	90		
27	6:59	312	.831	110	33.60	1.4663
28	7:11	305	.818	80		
29	7:25	306	.806	65	45.70	1.4560
30	7:40	310	.808	58		
31	7:53	302	.803	40		
32	8:05	303	.800	29		
33	8:30	313	.807	55	51.80	1.4531

Residue 510 cc.

Loss 350 cc.

TABLE XVI.

RUN #10

Time.	Temp.	Sp. Gr.	Vol.	% Vol.	Br.	N
2:35	51	0.656	110	6.7	1.72	1.3779
2:40	71	0.667	215	13.2	1.23	1.3803
2:45	85	0.686	210	13.0	1.55	1.3877
2:50	98	0.710	205	12.7	3.14	1.3978
3:00	110	0.726	195	12.4	1.49	1.4035
3:05	119	0.742	190	10.4	1.86	1.4131
3:10	126	0.748	105	6.4	1.20	1.4169
3:15	133	0.754	105	6.4		1.4207
3:20	140	0.759	70		1.63	1.
3:30	149	0.762	75			
4:00	200	0.775	170		1.56	1.4285

RUN #11.

10:43	100	0.723	290	13.7	5.45	1.4042
10:48	113	0.735	168	8.0	5.37	1.4076
10:52	118	0.741	150	7.12	5.30	1.4110
10:56	123	0.746	162	7.61	5.45	1.4141
11:00	127	0.751	140	6.64	5.42	1.4166
11:04	131	0.756	120	5.61		
11:08	135	0.759	105	4.92	6.05	1.4198
11:15	141	0.764	145	7.06		
11:26	149	0.768	150	7.12	5.85	1.4230
11:39	168	0.785	405	19.1	5.61	1.4355
11:52	200	0.802	220	10.4		1.4445
12:15	270	0.815	60	2.3	5.56	1.4532

Motor spirit of sp.gr. 0.764. First distillate over at 83°.